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THE APPLICATION OF DARK-FIELD ELECTRON MICROSCOPY TO THE DETERMINATION OF CRYSTALLITE SIZE IN FERRITES

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The application of dark-field electron microscopy to the determination of crystallite size in ferrites

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Abstract

Barium and strontium ferrites were prepared by coprecipitation from nitrate solutions, filtering and calcining at 1100°C or 1300°C. The calcined powders were ground in a steel mortar. A method was developed for supporting the powders in thin plastic films for electron microscopy. Powders were examined by electron microscopy in bright and dark fields, and by electron diffraction.

Three types of particle in the micron range of size were found, two being monocrystalline and one finely polycrystalline with a crystallite size of about 500Å. It was not possible to distinguish between these particles without the use of electron diffraction.

It was found that the grains of the barium ferrites were generally smaller than those of the strontium ferrites prepared under similar conditions, and that the grain sizes of both increased with calcining temperature.

Introduction

Crystals of hexagonal ferrites of the type (Ba, Sr, Pb)0.nFe_2O_3, where n is about 6, show a strong magnetic anisotropy which makes them useful for production of permanent magents. The energy product (BH)max of these magnets can be improved by orienting all the crystals in one direction by applying a magnetic field during the forming process. For ideal orientation, each grain of the powder should be a single crystal(1).

The coercive force of the magnets is partly dependent on the grain size. For barium ferrite, the critical particle diameter is about 1.3μ(2), so that the starting material for a magnet should consist of separate single crystals of about 1μ diameter.

For these reasons it is important to know the size of the crystallites in the starting powder and whether they are, in fact, single crystals.

Since the particles are magnetic at normal temperatures, they attract each other and form aggregates larger than the individual crystallites, so that methods for determining the crystallite size, such as measurements of settling rates in liquids, are not suitable.

The application of X-ray line broadening to particle size determination for these materials is not reliable since it is complicated by the presence of preferred orientation and by the closeness of the ferrite lines to those of the oxides and carbonates from which they are made.

Electron microscopy enables the particles to be seen and their size measured; dark-field electron microscopy and electron diffraction enable one to determine whether or not a particle is a single crystal, and, if it is polycrystalline, the size of the individual crystals can be determined. The application of the method is limited to those crystals that are transparent to electrons, that is, usually less than ½μ thick.

The principle of the method is shown in Fig. 1. In passing through the crystal (S), the electron beam is split into a main beam and a series of diffracted beams whose directions depend on the crystal structure and orientation in the same way as in X-ray diffraction. All these beams are focussed by the objective lens of the

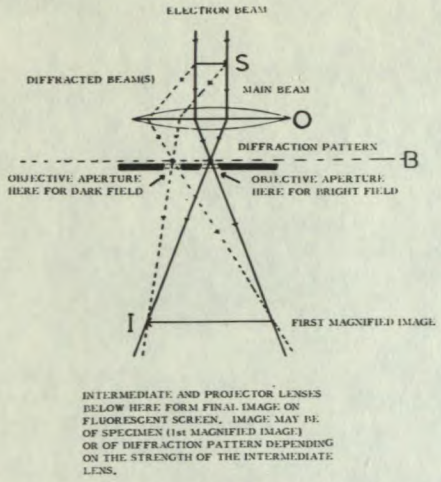

Fig. 1 Principle of dark field microscopy.

microscope (O), so that a diffraction pattern is produced in the back focal plane of the objective (B), in addition to a series of magnified images from all the beams at I. For normal microscopy, an aperture is inserted at B to cut out all except the main beam; the other two lenses of the microscope form a final magnified image of the object with this main beam. The power of these two lenses can be adjusted to focus the diffraction pattern instead of the image on the final screen.

For the dark-field image, the aperture is moved so as to let one of the diffracted beams through instead of the main beam, and an image is formed with this diffracted beam, which corresponds to the portions of the specimen contributing to that particular diffraction maximum, and, therefore, in one particular orientation. The spread of orientations observed is determined by the size of the aperture.

Thus, the part of a single crystal which contributes to a particular reflection or, in a powder, those grains near to one particular orientation, may be imaged. By examining the diffraction pattern and dark-field images, it is possible to determine whether a grain is a single crystal or a powder aggregate and, if a powder, the size of the particles. The smallest area that can be examined is about 1000Å in diameter. The technique is described in more detail in standard works on electron microscopy(3).

Experimental procedures

1. Sample Preparation: Samples were prepared by the co-precipitation method from reagent-grade barium, strontium and iron nitrates. Mixed nitrate solutions of appropriate compositions were sprayed into water in a precipitation tank. Carbon dioxide and ammonia gas were bubbled through the water to maintain the pH of the slurry at about eight. Excess CO_2 was used to ensure complete precipitation of the barium or strontium as carbonates. The temperature was maintained at 65°C. When the supernatant liquid showed no more metal ions in solution, the slurry was filtered, and the residue washed, dried at 110°C, mixed in a mortar and analyzed for iron and barium or strontium.

About five gram samples were then calcined at 1100°C and 1300°C for about half-an-hour.

2. Examination of the powders: The calcined samples were then examined by X-ray diffraction using both Debye - Scherrer and diffractometer methods.

For electron microscopy, the powders were first ground in an agate mortar. It was found that they could not be dispersed properly by ultrasonic vibration since they quickly reformed magnetic aggregates too large for examination before they could be but on to specimen supporting films. Further, since they are magnetic, it was considered desirable to have them actually embedded in a thin plastic supporting film so that they would not be pulled off by the magnetic field of the objective lens. The following procedure was therefore developed.

Small amounts of powder were ground in a steel mortar, the pestle removed and most of the powder blown out of the mortar. Enough powder was left adhering to the mortar to use for a sample. A drop of 0.5% solution of Formvar (a plastic) in ethylene dichloride was placed on the bottom of the mortar. The solvent evaporated leaving a Formvar film about 500Å thick over the particles. The Formvar film was backed by gently pressing cellulose acetate tape moistened with acetone onto it, and allowing this to dry. The double film was then peeled off, placed over specimen grids and put into an apparatus for slow removal of the acetate backing(4). A thin film of carbon was then evaporated on the Formvar film to give it stability in the electron beam. The film contained the particles from the mortar embedded in it so they could not move in the magnetic field of the microscope. Specimens were examined by bright- and dark-field microscopy and by electron diffraction.

Four samples were examined: $BaO.6Fe_2O_3$ calcined at 1100°C and at 1300°C, and $SrO.6Fe_2O_3$ calcined at 1100°C and at 1300°C.

Experimental results

The lack of metallic ions in the supernatant liquid indicated that the co-precipitation process was quantitatively complete. However, optical microscopy of the co-precipitated powder showed some crystals of barium and strontium carbonates about 3μ in size. Surface area measurements of the powder gave values of 30-40 m^2/g which is equivalent to a particle size of about 100Å. This wide spread in particle size could lead to segregation in the slurry during settling, indicating the necessity of proper mixing before calcining in order to ensure homogeneity.

X-ray diffraction patterns showed traces of Fe_2O_3 to be present in the samples calcined at 1100°C, but not in those calcined at 1300°C. Broadening the lines suggested a particle size below 1μ but some spots were observed in the lines of the pattern from the barium ferrite calcined at 1300°C, indicating substantial grain growth.

Only particles thin enough to be transparent to the electron beam could be properly examined by electron diffraction and dark-field electron

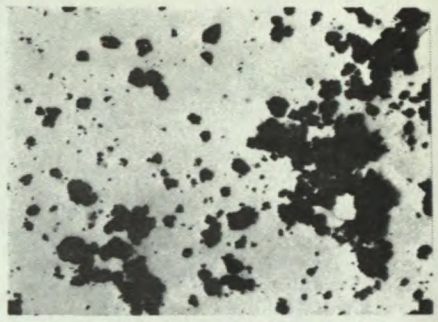

Fig. 2. Particles of barium ferrite calcined at 1100°C. (X10,000)

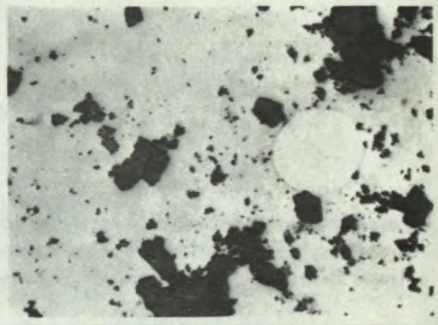

Fig. 3. Particles of barium ferrite calcined at 1300°C. (X10,000)

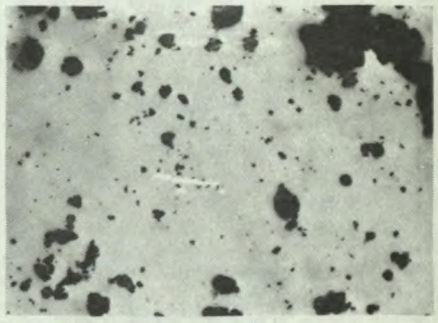

Fig. 4. Particles of strontium ferrite calcined at 1100°C. (X10,000)

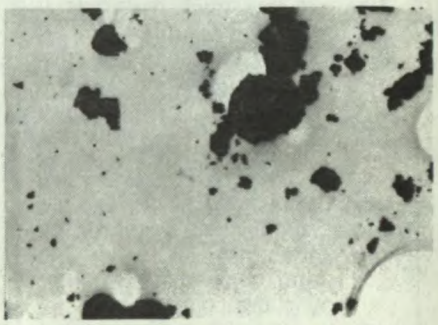

Fig. 5. Particles of strontium ferrite calcined at 1300°C. (X10,000)

microscopy; this represented only about 10% of the larger particles.

A large range of particle sizes, from a few hundred Angstroms to over one micron, was found for all samples (Figs. 2-5). There were many aggregates of particles about 1μ in diameter, but it was not possible to tell whether these were held together by magnetic attraction, by surface tension effects in the film or by sintering.

Examination of the particles in the size range above 0.25μ revealed three types of particle shown in Figs. 6-9.

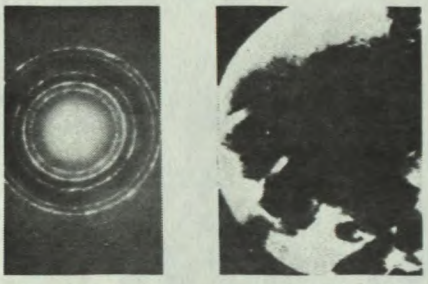

Fig. 6. Diffraction pattern and bright-field micrograph of polycrystalline aggregate in strontium ferrite calcined at 1300°C. (X100,000)

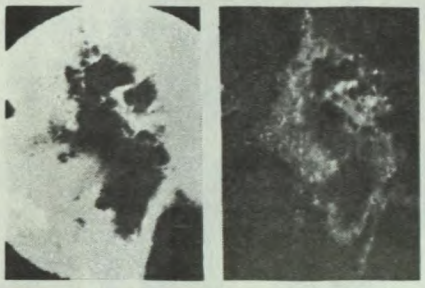

Fig. 7. Bright- and dark-field micrographs of polycrystalline aggregate in strontium ferrite calcined at 1300° (X100,000)

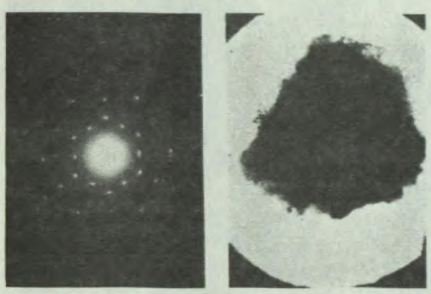

Fig. 8. Diffraction pattern and bright-field micrograph of single crystal of barium ferrite having appearance similar to polycrystalline aggregates calcined at 1300°C. (X100,000)

Fig. 9. Idiomorphic single crystal of barium ferrite calcined at 1300°C. (a) dark-field micrograph (X50,000) (b) bright-field (X100,000)

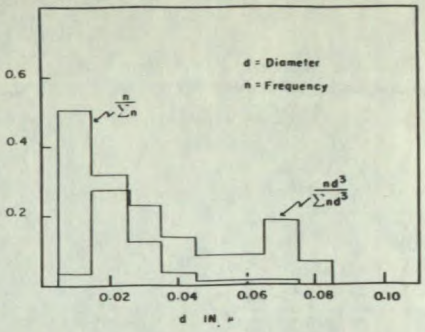

Fig. 10. Crystalline size distribution in polycrystalline aggregates in barium ferrite.

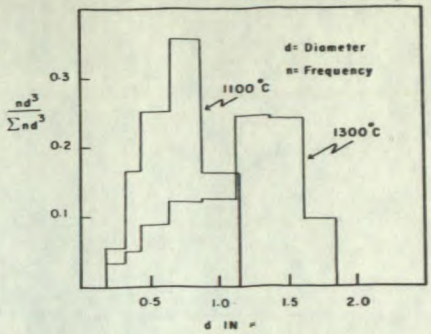

Fig. 11. Particle size distribution of barium ferrite.

The type least expected is shown in Fig. 6. The electron diffraction pattern is a powder pattern showing that the particle is made up of a random array of small crystallites. The pattern corresponds to that of strontium ferrite. Fig. 7 shows bright- and dark-field pictures of a similar particle, showing a crystallite size range of 100-600Å. It can be seen that the thinner parts of the bright-field picture (b) also show granularity of a size comparable with the crystallite size. It was also found that many of the larger particles in the micron range had small crystallites attached to their surfaces.

Fig. 8 shows a type of particle which has a similar appearance to the powder aggregates described above; however, its diffraction pattern shows that it is a single crystal. Close examination reveals no granular structure similar to that visible in Fig. 7 but, at low magnification, it would be difficult to distinguish these single crystals from the powder aggregates by appearance alone.

Also present were idiomorphic single crystals of the type shown in Fig. 9 in bright and dark field. Some structures which may be arrays of of these crystals showed internal dislocations.

Histograms showing the distributions of crystallite size and weight of the polycrystalline particles of the type shown in Figs. 6-7 are shown in Fig. 10.

Particle size distributions were measured for the four samples. A histogram of weight distribution for $BaO.6Fe_2O_3$ is shown in Fig. 11. The particles are shown in Figs. 2 and 3. The results showed an increase in particle size for the higher calcining temperature, the sizes associated with the average weight particles were 0.6μ and 1.1μ for 1100°C and 1300°C, respectively.

The results for $SrO.6Fe_2O_3$ were similar, except that the particle size was larger than for the barium ferrite. Particles are shown in Figs. 4 and 5. The sizes of the average weight particles were 1.1μ for 1100°C and 1.6μ for 1300°C.

Conclusions

Three types of particles in the micron range of size were found, two monocrystalline and one finely polycrystalline. The single crystals showed the the polycrystals showed a powder hexagonal symmetry of the ferrites; pattern of the ferrite. It is not clear how these powder aggregates form but their particle size (Fig. 10) is about that of the Fe_2O_3 prior to calcining, whereas the single crystals are nearer in size to those of the original barium or strontium carbonate. Further, the presence of the tiny crystallites on the surface of the larger grains suggests that they may have been formed from the Fe_2O_3.

Unfortunately, since the various types of particle could not be distinguished by shape alone, it was not possible to determine the relative numbers of the various types since most were not transparent to electrons. Thus, although the particle sizes showed an increase at higher calcining temperatures, it was not possible to determine whether the percentage of polycrystalline particles changed.

The measurements showed that the particle size of the strontium ferrite was greater than that of the barium ferrite for both calcining temperatures. These measurements may be only comparative since the technique of preparation of the electron microscopy specimens tends to favour smaller particles. This would not affect the measurement size range, since most large particles seem to be aggregates of smaller crystals in the micron range, but it would affect the measurements of size distribution.

Acknowledgements

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